KFKI-71-70

B. Gellai
G. Jancsó

APPLICATION OF THE MINIMAX APPROXIMATION TO THE ISOTOPE EFFECT ON HEAT CAPACITY OF IDEAL GASES

Hungarian Academy of Sciences

CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS

BUDAPEST

KFKI-71-70

APPLICATION OF THE MINIMAX APPROXIMATION TO THE ISOTOPE EFFECT ON HEAT CAPACITY OF IDEAL GASES

B.Gellai, G.Jancsó

Central Research Institute for Physics, Budapest, Hungary
Chemistry Department

ABSTRACT

The minimax approximation to the isotope effect on heat capacity of ideal gas molecules is worked out. The rate of convergence and the utility of this approximation are discussed by means of numerical calculations for various polyatomic molecules and the results compared with those obtained by other approximations.

KIVONAT

Kidolgoztuk az ideális gázok fajhőjében az izotóphelyettesités által előidézett effektus minimax közelitését. A módszer konvergenciasebességét és alkalmazhatóságát különböző izotópmolekulapárokon végzett számitásokkal vizsgáltuk meg és a kapott eredményeket összehasonlitottuk más közelitésekkel nyert eredményekkel.

РЕЗЮМЕ

Был разработан метод "минимаксного" приближения для эффекта, вызванного изотопным замещением в теплоемкости многоатомных идеальных газов. С целью исследования скорости конвергентности и применяемости метода были произведены подсчеты для различных пар изотопных аналогов, и полученные результаты сравнивались с результатами других приближений.

INTRODUCTION

In three previous publications [1,2,3] minimax approximations have been worked out for the reduced partition function ratio of isotopic molecules and for the specific heat of crystals. From the reduced partition function ratio one can derive formulas for the effect of isotopic substitution on the thermodynamic functions of ideal gases. In the present work the minimax approximation to the isotope effect on heat capacity /IEHC/ of ideal gas molecules is described and its usefulness in practical calculations analysed by means of numerical calculations for various polyatomic molecules.

METHOD AND RESULTS

The IEHC of ideal gases is related to the reduced partition function ratio of isotopic molecules by the following equation [4]:

$$\Delta C_r^o = R \frac{\partial}{\partial T} \left\{ T^2 \frac{\partial}{\partial T} \ln\left(\frac{s}{s'} f\right) \right\} \qquad /1/$$

where ΔC_r^o is the reduced difference in heat capacity of isotopic molecules, and $(s/s')f$ is the reduced partition function ratio of isotopic molecules, as introduced by Bigeleisen and Mayer [5]. If correction for non-classical rotation are negligible Eq. /1/ yields, in the harmonic oscillator - rigid rotator approximation [6]:

$$\frac{\Delta C_r^o}{R} = \sum_{i=1}^{3N-6} \left\{ u_i^2 \, e^{u_i} / \left(e^{u_i}-1\right)^2 - u_i'^2 \, e^{u_i'} / \left(e^{u_i'}-1\right)^2 \right\} =$$

$$= \sum_{i=1}^{3N-6} \left\{ \frac{(u_i/2)^2}{\mathrm{sh}^2(u_i/2)} - \frac{(u_i'/2)^2}{\mathrm{sh}^2(u_i'/2)} \right\} \qquad /2/$$

where $u_i = hc\omega_i/kT$. ω_i is the i-th normal vibrational frequency /in cm^{-1}/, 3N-6 is the number of internal degrees of freedom for a molecule with N atoms /3N-5 for a linear molecule/, while u_i' and u_i stand for light and heavy isotopic species, respectively.

The expression $(u_i/2)^2/\ sh^2 u_i/2$ on the r.h.s. of Eq. /2/ corresponds to the function G/ux/

$$G(ux) = \left(\frac{ux}{sh(ux)}\right)^2 \qquad /3/$$

in Eq./5/ used for the evaluation of specific heat of crystals [3], if $ux = u_i/2$. The minimax approximation to the function G/ux/ can therefore be applied in the minimax approximation to the IEHC of ideal gas molecules:

$$\frac{\Delta C_r^o}{R} = \sum_{k=o}^{n} a^*\left(n,k,u_{max}\right) \sum_{i=1}^{3N-6} \delta\left(u_i/u_{max}\right)^{2k} \qquad /4/$$

where $a^*/n,k,u_{max}/$ are the coefficients of the minimax approximation to G/ux/ [3]; and $\delta(u_i/u_{max})^{2k} = \left(\frac{u_i - u_i'}{u_{max}}\right)^{2k}$.

In calculations with Eq. /4/ a common u_{max}, determined by the highest frequency of the light isotopic molecule, was used for the isotopically different molecules. For exact calculation of $\Delta C_r^o/R$ the individual molecular frequencies were evaluated by the Wilson FG-matrix method [7].

The results obtained with the minimax approximation /Eq. /4// for deuterated methylfluoride are presented in Table I along with the exact values of $\Delta C_r^o/R$ /Eq./2//. It can be seen that the minimax approximation to $\Delta C_r^o/R$ gives substantially worse results than those obtained for the minimax approximation to ln(s/s')f [1,2]. /The same was found in a l other calculations carried out for isotopic pairs of molecules./ Th s is not surprising if one considers that even the minimax approximation to G/ux/ only gives good results for practical calculations at high values of u_{max} if high order polynomials are used. Furthermore, the approximation may be worsened by unfavourable error summation which can occur in forming the difference in the heat capacities of isotopic molecules.

Another approximation to $\Delta C_r^o/R$ can be derived by differentiating the minimax approximation to the reduced partition function ratio. One obtains

$$\frac{\Delta C_r^o}{R} = \sum_{k=1}^{n} 2k(2k-1)\, a\left(n,k,u_{max}\right) \sum_{i=1}^{3N-6} \delta \left(u_i/u_{max}\right)^{2k} \qquad /5/$$

where $a\ /n,k,u_{max}/$ are the coefficients of the minimax approximation to $\ln\ b/u/$ [1,2]:

$$\ln b(u) = \sum_{k=o}^{n} a\left(n,k,u_{max}\right)\left(\frac{u}{u_{max}}\right)^{2k} \qquad /6/$$

For the monodeuteromethane molecule the results of the minimax approximation to the IEHC /Eq. /4// are compared with those obtained with Eq. /5/ in Table II. Also shown are the results of the approximation to $\Delta C_r^o/R$ derived by Bigeleisen [6]:

$$\frac{\Delta C_r^o}{R} = \sum_{i=1}^{3N-6} C(u_i)\ \Delta u_i \qquad /7/$$

where

$$C(u_i) \equiv \frac{2u_i^2\, e^{2u_i}}{\left(e^{u_i}-1\right)^3} - \frac{u_i\left(u_i+2\right)e^{u_i}}{\left(e^{u_i}-1\right)^2} \qquad /8/$$

and $\Delta u_i = u_i' - u_i$. Values of the function $C/u_i/$ have been tabulated for different u_i [6]. Inspection of the values in Table II shows that the minimax approximation to $\Delta C_r^o/R$ /Eq. /4// gives better results than those obtained from the minimax approximation to the reduced partition function ratio of isotopic molecules /Eq. /5//. The Bigeleisen approximation /Eq. /7// also has too high error values in this particular example, and thus cannot be used for practical evaluation of $\Delta C_r^o/R$ for molecules of the above type.

The cont ibutions of the various molecular frequencies to the IEHC of ideal methanol molecules are presented in Table III. Those frequencies for which $u_i' > \sim 10$ clearly contribute only slightly to the heat capacity difference between CH_3OD and CH_3OH at 200 and 300°K.

Consequently, it is permissible to cut off the approximation at these frequencies and in this way avoid errors caused by the unnecessarily large range of the approximation.

Results for isotopic methanol molecules obtained using coefficients of the minimax approximations /Eq. /4// given by using exact values of u_{max} and by cutting off the frequencies for which $u_i' > 12$ are compared in Table IV. It can be seen that the "cut off" procedure significantly improves the results of the minimax approximation. Because of the relatively small number of terms involved it may thus be applied advantageously to obtain practically useful approximations to $\Delta C_r^o/R$ at lower temperatures.

Table I.

Approximation to $\Delta C_r^o/R$ by the minimax method for deuterated methyl fluoride[1]

T_{o_K}	200	300	400	1200	3000
U_{max}	22.78	15.19	11.39	3.80	1.52
Exact $\Delta C_r^o/R$	0.156620	0.605936	0.950475	1.035245	0.300139
Minimax approximation			Percent error		
n = 1[2]	-89.1	-59.8	-39.8	-7.66	5.49
n = 2	-147	67.5	50.2	1.10	-0.120
n = 3	-87.7	-14.1	9.96	0.502	-0.001
n = 4	-87.9	-62.1	-32.5	-0.063	0.000
n = 5	-32.7	-26.0	-10.6	-0.008	0.000
n = 6	-152	6.41	-0.862	-0.001	-0.000
n = 7	-148	20.9	2.00	0.000	-0.000
n = 8	169	13.2	1.38	0.000	-0.000

1 F matrix elements taken from [8], geometrical parameters as given in [8].

2 n the order of expansion

Table II.

Comparison of various expansions of $\Delta C_r^o/R$ for methane - d_1.[1]

$T\ ^oK$	300	400	800	1200	3000
U_{max}	15.12	11.34	5.67	3.78	1.51
Exact $\Delta C_r^o/R$	0.103374	0.198435	0.353167	0.317896	0.096614
Minimax approximation			Percent error		
n = 1	-78.8[2]	-61.3	-25.8	-12.6	4.62
	-98.1	-94.6	-72.0	-48.9	-10.6
n = 2	340	65.0	4.14	0.514	-0.201
	-101	-104	-259.5	41.9	0.246
n = 3	-10.8	12.5	2.91	0.435	-0.003
	-99.2	-96.0	-35.0	-4.63	0.012
n = 4	-72.7	-40.7	-0.23	-0.076	0.000
	-101	-110	10.55	0.429	-0.000
n = 5	-3.20	-6.47	-0.160	-0.006	0.000
	-95.9	-71.9	-0.790	-0.017	-0.000
n = 6	61.4	3.52	-0.009	-0.000	-0.000
	-150	29.0	0.006	-0.000	0.000
n = 7	75.6	5.28	0.007	0.000	-0.000
	-145	40.2	0.031	0.000	-0.000
n = 8	19.6	2.03	0.002	0.000	-0.000
	-84.9	-25.5	-0.012	-0.000	-0.000
Approximation Eq. (7)	-45.0	-34.1	-26.6	-14.1	10.6

1 F matrix elements and geometrical parameters taken from [9]

2 For each temperature and order the upper number is calculated using Eq. (4), the lower using Eq. (5).

Table III.

The contributions of various molecular frequencies to the heat capacity difference between CH_3OH and CH_3OD[1,2]

		200°K			300°K		
ν_i	ν_i'	u_i	u_i'	$\Delta C^o_{r,i}$[3]	u_i	u_i'	$\Delta C^o_{r,i}$[3]
2992.080	3705.065	21.520	26.649	$2.07 \cdot 10^{-7}$	14.347	17.766	$1.15 \cdot 10^{-4}$
2865.746	2992.139	20.612	21.521	$2.66 \cdot 10^{-7}$	13.741	14.347	$8.24 \cdot 10^{-5}$
2715.165	2864.963	19.529	20.606	$7.82 \cdot 10^{-7}$	13.019	13.737	$1.72 \cdot 10^{-4}$
1458.093	1462.932	10.487	10.522	$8.52 \cdot 10^{-5}$	6.992	7.015	$7.42 \cdot 10^{-4}$
1430.077	1431.285	10.286	10.295	$2.52 \cdot 10^{-5}$	6.857	6.863	$2.04 \cdot 10^{-4}$
1227.925	1348.241	8.832	9.697	$5.51 \cdot 10^{-3}$	5.888	6.465	$3.14 \cdot 10^{-2}$
1048.284	1091.092	7.540	7.848	$6.17 \cdot 10^{-3}$	5.027	5.232	$2.01 \cdot 10^{-2}$
870.535	1035.954	6.261	7.451	$4.28 \cdot 10^{-2}$	4.174	4.967	$1.02 \cdot 10^{-1}$
2992.441	2992.441	21.523	21.523	0.0	14.349	14.349	0.0
1477.111	1477.111	10.624	10.624	0.0	7.083	7.083	0.0
1157.439	1157.439	8.325	8.325	0.0	5.550	5.550	0.0
$\Sigma\Delta C^o_{r,i}$				$5.473 \cdot 10^{-2}$			$1.552 \cdot 10^{-1}$

1 F matrix elements taken from [10], geometrical parameters from [11].

2 The contribution from hindered rotation of the OH group is not included in $\Sigma\Delta C^o_{r,i}$

3 The values of $\Delta C^o_{r,i}$ were calculated from Eq. (2).

Table IV.

Comparison of the approximations to $\Delta C_r^o/R$ for isotopic methanol molecules with the actual U_{max} and "cut off" U_{max}. ($T = 300^oK$[1])

	PERCENT ERROR							
n	1	2	3	4	5	6	7	8
$CH_3OH - CH_3OD$	-65.9[2]	-151	-42.9	-55.2	-37.4	-13.8	3.63	-16.8
	-39.8	-37.3	3.20	4.90	0.876	0.551	0.180	0.153
$CH_3OH - CD_3OH$	-37.3	-48.3	46.1	-18.3	-52.5	-35.6	11.2	19.9
	54.7	-35.6	28.6	5.75	0.710	1.67	1.49	1.54
$CH_3OH - CD_3OD$	-45.8	-16.2	14.8	-29.7	-50.0	-32.5	10.3	10.6
	-52.1	-36.2	23.5	6.12	0.425	1.29	1.28	1.29
$^{12}CH_3OH - {}^{13}CH_3OH$	2.72	-8.07	-20.5	-56.6	-48.8	7.52	3.37	-6.25
	-58.0	-32.0	19.0	2.73	2.11	-0.210	-0.394	0.138
$CH_3{}^{16}OH - CH_3{}^{18}OH$	48.6	1825	-62.9	85.7	-60.1	26.1	-29.4	10.3
	-41.1	-41.4	0.170	9.63	2.25	-0.385	-0.384	-0.022

1 See footnotes 1,2 of Table III.

2 For each pair of isotopic molecules and each order the upper number is calculated using the actual value of U_{max} the lower using the cut-off value of U_{max}.

REFERENCES

[1] G. Németh, B. Gellai, G. Jancsó, KFKI Report 15, 1970, Budapest

[2] G. Németh, B. Gellai, G. Jancsó, J. Chem.Phys. 54, 1701 /1971/

[3] G. Jancsó, G. Németh, B. Gellai, Chem. Phys. Letters, 7, 314 /1970/

[4] G. Vojta, Z. physik. Chemie /Leipzig/ 217, 337 /1961/

[5] J. Bigeleisen, M.G. Mayer, J. Chem.Phys. 15, 261 /1947/

[6] J. Bigeleisen, J. Chem.Phys. 21, 1333 /1953/

[7] E.B. Wilson, J.C. Decius, P.C. Cross, Molecular Vibrations, McGraw-Hill Book Co., New York, 1955

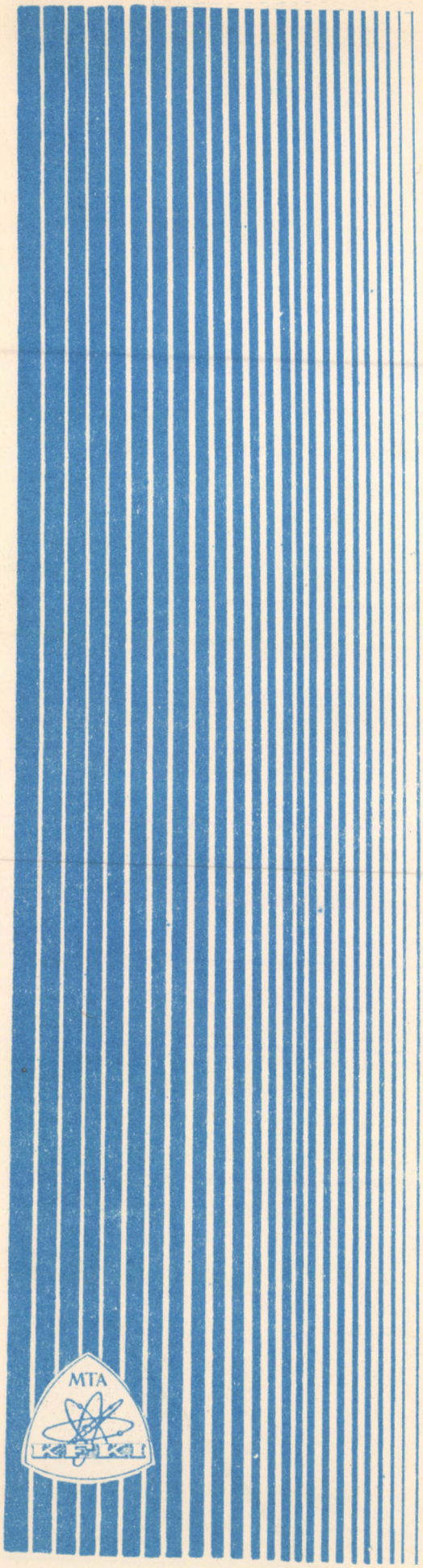
[8] G. Jancso, B. Gellai, KFKI Közlemények 16, 181 /1968/

[9] L.H. Jones, R.S. McDowell, J. Mol. Spectr. 3, 632 /1959/

[10] B. Gellai, G. Jancsó, unpublished results

[11] P. Venkateswarlu, W. Gordy, J. Chem.Phys. 23, 1200 /1955/

61.926



Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Szabó Elek, a KFKI
Kémiai Tudományos Tanácsának elnöke
Szakmai lektor: Kósa Somogyi István
Nyelvi lektor: T. Wilkinson
Példányszám: 195 Törzsszám: 71-6167
Készült a KFKI sokszorosító üzemében,
Budapest
1971. december hó